

Research, Experimental Development, and Application of Alpha-Ketoglutaric Acid as a Decontaminant for Hazardous Fluids

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In 2008, NASA Kennedy Space Center (KSC) became interested in alpha-ketoglutaric acid (AKGA) for monomethylhydrazine (MMH) and hydrazine decontamination because of its potential cost and operational benefits. Also, AKGA has gained attention for the potential decontamination of space shuttles for museums or other displays because of the reduced safety and health risks of its by-products. NASA Johnson Space Center's White Sands Test Facility (WSTF) collaborated with NASA Engineering and Safety Center in an assessment of AKGA use for treatment of hydrazine- and MMH-contaminated hardware, hardware decommissioning, and reduction of hydrazine and MMH waste streams. Although that assessment reported low technology readiness levels at that time, WSTF anticipated further evaluation and performed a literature survey and laboratory investigations with AKGA, hydrazine, and MMH to characterize AKGA reactions. WSTF also conducted a decontamination evaluation on a space shuttle orbiter Forward Reaction Control System (FRCS) test article.

Research and Experimental Development

The literature research yielded a limited amount of data on the reaction of AKGA with hydrazine or MMH, but provided an excellent baseline for investigative work. WSTF performed multiple experiments designed to provide a fundamental understanding of AKGA-hydrazine and AKGA-MMH reaction chemistry not found in the literature. Experiments included pH measurements, reaction characteristics and rates under stoichiometric conditions, concentration effects, open beaker screening tests, and vapor measurements on AKGA-treated hydrazine- and MMH-contaminated soft-goods material. Studies were also performed using 1.0 M (moles per liter) AKGA to determine corrosion rates of selected alloys commonly used in aerospace applications.

The reaction of AKGA with hydrazine produces 1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (PCA) and water, and with MMH produces 1-methyl-1,4,5,6-tetrahydro-6-oxo-3-pyridazinecarboxylic acid (MPCA) and water. Reaction rates and completeness of

reactions are concentration dependent. AKGA solutions are acidic and must be handled with appropriate safety precautions. When pure hydrazine and AKGA are combined, the reaction of hydrazine evolves gas and is sufficiently exothermic that the fuel must be diluted for safety reasons. Similar precautions should be applied to MMH although no heating or gas evolution was observed.

MMH-contaminated polytetrafluoroethylene (PTFE) was not decontaminated by AKGA. Corrosion rates were obtained for stainless steel (SS) 304, SS 316, 17-4, MP35, Inconel® 718, and titanium (Ti) 6-4 in 1.0 M AKGA and were in low microinch per year ($\mu\text{in}/\text{yr}$) ranges, considered acceptable for decommissioned but not reusable hardware. If hardware is reused, the corrosive nature of AKGA must be considered during the refurbishment process to ensure that surface characteristics, compositions, and tolerances are acceptable. Corrosion rates must also be taken into account for the determination of AKGA soak times so as not to corrode hardware beyond acceptable limits. Note: During the initial investigation, no characterizations were performed at WSTF with 4.0 M AKGA, which was the most concentrated solution evaluated by KSC.

It was thought that AKGA may be well suited to the control of hydrazine and MMH spills because it is relatively nontoxic, does not ignite, does not produce volatile halogenated products, and forms stable products. When a stoichiometric excess of AKGA is used, it favors rapid and complete reactions. It was recommended that AKGA be examined as a spill control agent for hydrazine and MMH at WSTF, and that lab and field experiments be performed to establish optimum fuel dilution and AKGA concentrations and to develop written spill procedures, and the use of AKGA be considered as a potential means for eliminating hydrazine and MMH waste streams. This was one of the primary reasons for KSC interest in AKGA.

Experimental Application

When KSC took the lead to examine 4.0 M AKGA for decontamination and decommissioning of hydrazine- and MMH-contaminated flight hardware, tests at WSTF were performed using 4.0 M AKGA. Two MMH-contaminated

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continued

test articles were taken from the Fleet Leader FRCS pod at WSTF. The test articles (manifolds and lines previously decontaminated during FRCS disassembly) were modified with fittings that allowed the test articles to be readily sealed and filled with AKGA solutions. The fittings were designed to also serve as sampling ports to accept Dräger Pac III[®] hydrazine vapor monitors for MMH vapor measurements (figure 1). The test articles were purged with gaseous nitrogen gas for 6 and 8 days, respectively, to ensure they were free of detectable residual MMH vapor. Nitrogen gas effluent was monitored at each exit orifice using the vapor monitors. The pretest MMH vapor concentration in Test Article #1 registered 340 parts per billion (ppb) after 30 minutes; in Test Article #2, vapor concentration fluctuated between zero and 10 ppb after 24 hours.

Both test articles were filled with 4.0 M AKGA from the same source that KSC used; Test Article #1 remained filled for 125 days and Test Article #2 remained filled for 119 days. On Test Article #1, brown liquid leaked from a flange 11 days after testing was initiated, and solidified within 2 days (figure 2). The crystals were analytically determined to be AKGA.

After the AKGA was drained, the test articles were flushed with deionized water to remove residual detectable AKGA to below 1.0 part per million (ppm) as determined by liquid chromatography, then flushed with gaseous nitrogen to remove residual water. Test Article #2, however, continued to maintain residual AKGA concentrations above 1.0 ppm and therefore was not subject to subsequent steps, and no posttest vapor concentration measurements were taken. The AKGA foamed when drained, and care was taken because pressure had built up from reactions with the metals in the test articles.

Dissolved metals from the posttest fluids were determined by inductively coupled plasma mass spectrometry. To investigate the corrosion of the FRCS test article line materials (a combination of stainless steels including 304, 316, 321, and 17/7), correlating amounts of iron, chromium, and nickel powders were immersed in 4.0 M AKGA solutions and monitored visually for color

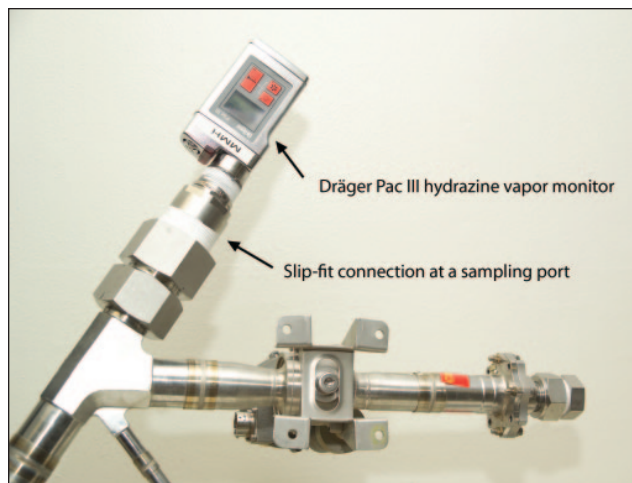


Fig. 1. Dräger Pac III[®] hydrazine vapor monitor affixed to Forward Reaction Control System test article.



Fig. 2. Crystallized material on test article flange.

change. Results are shown in figure 3. The colors of the solutions were also compared to solutions of equivalent concentrations prepared from the addition of iron(II) sulfate heptahydrate, chromium(III) nitrate nonahydrate, and nickel(II) nitrate hexahydrate dissolved in 4.0 M AKGA solution.



Fig. 3. Appearance of pretest 4.0 M alpha-ketoglutaric acid (AKGA), and iron, chromium, nickel powders in 4.0 M AKGA, and posttest 4.0 M AKGA.

Conclusions

Laboratory investigations found that reactions of AKGA with hydrazine and MMH produce PCA and MPCA, respectively. AKGA solutions are acidic and must be handled with safety precautions. AKGA-hydrazine reaction evolves gas sufficiently exothermic that the fuel must be diluted for safety. It was also found that MMH contaminated PTFE was not decontaminated by AKGA. Corrosion rates of relevant metals in 1.0 M AKGA were low enough to use for decommissioned but not reusable hardware.

AKGA may be well suited to the control of hydrazine and MMH spills and waste streams because it is relatively nontoxic, does not ignite, does not produce volatile halogenated products, and forms stable products. When a stoichiometric excess of AKGA is used, it favors rapid and complete reactions. Further investigation is strongly recommended.

The investigation of AKGA as a decontaminant fluid for decommissioned MMH contaminated flight hardware found that 4.0 M AKGA was not successful. The reduction of MMH vapor achieved could be due to factors other than the reaction with AKGA. AKGA is known to not be effective in decontaminating soft goods, and test data

show that 4.0 M AKGA is significantly corrosive toward the stainless steel alloys. The practical implications are that 4.0 M AKGA is not only corrosive to the FRCS metal components, but gas pressure can build up to the point where liquid inside the test article can be forcefully expelled. If there is no leak path, gas overpressure could result in component failure and consequential damage to hardware and potential injury to personnel.

The FRCS decontamination investigation concluded that residual MMH remains in the contaminated soft goods even after decommissioning decontamination, hardware corrosion will occur, and the use of 4.0 M AKGA could raise internal pressure due to gas evolution. Lastly, 4.0 M AKGA is a strong acid (pH 1.2) that requires appropriate safety precautions.